



COPY OF PAPERS
ORIGINALLY FILED

#29

(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
(Case No. 98,162)

In re Application of:

DeGendt, et al.

Serial No.: 09/022,834

Filed: February 13, 1998

For: METHOD FOR REMOVING ORGANIC
CONTAMINANTS FROM A
SEMICONDUCTOR SURFACE

Group Art Unit: 1746

Examiner: Ahmed

Commissioner of Patents
Washington, D.C. 20231

RECEIVED
JUL 02 2002
TC 1700

TRANSMITTAL LETTER

Dear Sir:

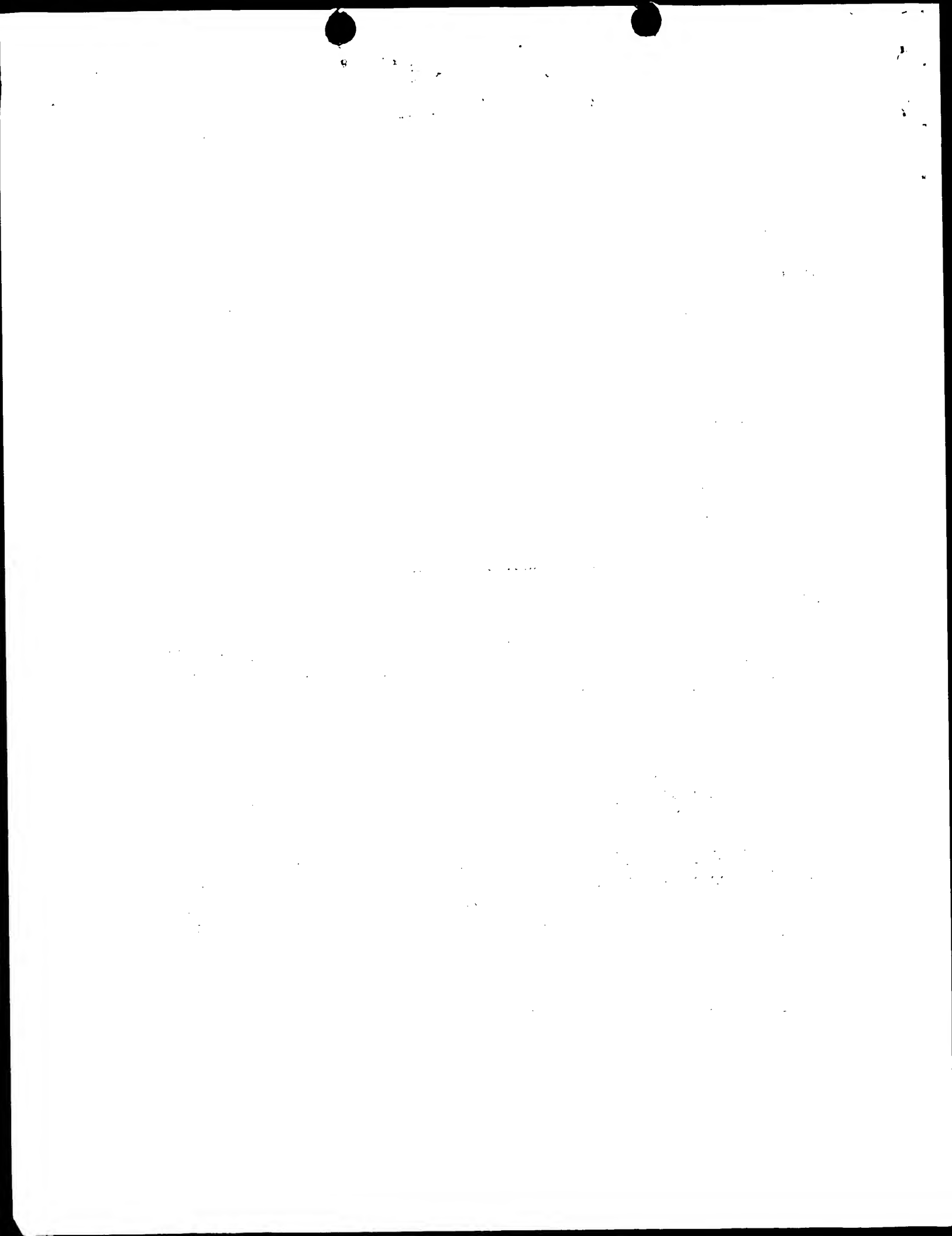
1. In regard to the above-identified Application, we are transmitting herewith the Submission of Certified Copy of Priority Document European Patent Application No. 98870056.3 and Return Receipt Postcard.
2. With respect to fees:
 - (a) No fee is required.
 - (b) Please charge any underpayment or credit any overpayment to our Deposit Account, No. 13-2490.
3. CERTIFICATE OF MAILING UNDER 37 CFR §1.8: The undersigned hereby certifies that this Transmittal Letter and the paper described in paragraph 1, are being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to Commissioner of Patents, Washington, D.C. 20231, on June 19, 2002.

DATED: June 19, 2002

BY:


Amir N. Penn

Registration No. 40,767





(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
(Case No. 98,162)

In re Application of:

DeGendt, et al.

Serial No.: 09/022,834

Filed: February 13, 1998

For: METHOD FOR REMOVING ORGANIC
CONTAMINANTS FROM A
SEMICONDUCTOR SURFACE

Group Art Unit: 1746

Examiner: Ahmed

RECEIVED
JUL 02 2002
TC 1700

Commissioner of Patents
Washington, D.C. 20231

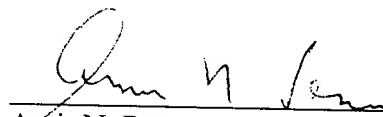
SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENT

Applicants submit herewith a certified copy of the priority document, European Patent Application No. 98870056.3, pursuant to 35 U.S.C. §119. Applicants respectfully request that the above-captioned application be afforded the benefit of the filing date of the European Patent Application.

Respectfully submitted,

DATED: June 19, 2002

BY:


Amir N. Penn
Registration No. 40,767



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets



Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

98870056.3

RECEIVED
JUL 02 2002
TC 1700

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

DEN HAAG, DEN
THE HAGUE, 06/06/02
LA HAYE, LE



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
Application no.: 98870056.3
Demande n°:

Anmeldetag:
Date of filing: 20/03/98
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM VZW
3001 Heverlee
BELGIUM

Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Method of removing a liquid from a surface of a rotating substrate

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: US
State:
Pays:

Tag: 24/09/97
Date:
Date:

Aktenzeichen:
File no.
Numéro de dépôt:

USA 59929

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:

H01L21/00

Am Anmeldetag benannte Vertragsstaaten:
Contracting states designated at date of filing:
Etats contractants désignés lors du dépôt:

AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE

Bemerkungen:
Remarks:
Remarques:

1. The first of these is the fact that the present movement is not a new one, but a continuation of the old one, which has been going on since the beginning of the world.

2. The second is the fact that the present movement is not a new one, but a continuation of the old one, which has been going on since the beginning of the world.

3. The third is the fact that the present movement is not a new one, but a continuation of the old one, which has been going on since the beginning of the world.

4. The fourth is the fact that the present movement is not a new one, but a continuation of the old one, which has been going on since the beginning of the world.

5. The fifth is the fact that the present movement is not a new one, but a continuation of the old one, which has been going on since the beginning of the world.

METHOD OF REMOVING A LIQUID FROM A SURFACE OF A ROTATING SUBSTRATE

FIELD OF THE INVENTION

5 The present invention is related to a method of removing a liquid from a rotating substrate. This liquid can be any wet processing liquid as e.g. a wet etching liquid or a cleaning liquid. It can also be a rinsing liquid. The invention is applicable for a number of wet processing steps which are frequently used in the fabrication process of
10 integrated circuits or liquid crystal displays.

BACKGROUND OF THE INVENTION

15 The complete and efficient removal of a liquid from a surface of a substrate is a multiply repeated step in e.g. the fabrication process of integrated circuits. Such a step can be performed after a wet etching step or a wet cleaning step or a wet rinsing step or any other step used in said fabrication process wherein said substrate is treated or exposed or immersed in a liquid. Said substrate can be a semiconductor wafer or a part thereof or a glass slice or any other slice of an insulating or conductive material.

20 The manufacturing of integrated circuits evolves towards processing of each substrate individually rather than in batches of several substrates. In state of the art IC manufacturing, most processing steps as e.g. implantation steps, deposition steps are already performed in a single substrate mode. On the other hand, wet processing steps
25 such as e.g. cleaning steps and subsequent liquid removal steps are typically performed in a batch mode because of lack of appropriate alternatives. Therefore, differences in waiting times are created for each individual substrate between a wet processing step, performed in a batch mode and another processing step, performed in a single substrate mode. Such variability is undesirable with regard to process control.
30 Moreover this mixed batch and single substrate processing increases the cycle time, which is also undesirable. Therefore, there is a general interest in the development of competitive single substrate wet processing steps. Particularly, one of the major challenges regarding single wafer wet processing is a method for removing a liquid from both sides of a substrate. There are two major requirements to be fulfilled for such a
35 method. At first the method should work sufficiently fast. Knowing that in state of the art production lines a substrate is processed typically every 2 to 3 minutes, ideally, in order to avoid equipment duplication, the process step and the liquid removal step should be completed in about such a time frame. Another requirement is related to the

preferred substrate orientation. State of the art processing equipment and transportation tools are developed to handle substrates in a horizontal position. Therefore in order to avoid additional substrate handling it would be desirable to perform the wet processing steps using horizontally positioned substrates.

5

In the European Patent EP 0 385 536 B1, a method is disclosed of drying substrates after treatment in a liquid by pulling said substrate slowly out of said liquid. However, this known method, which is based on the Marangoni principle, requires that the substrates are pulled out of the liquid in an upright position, i.e. a surface of said substrate is about perpendicular to the surface of the liquid bath as can be seen in figures 1 to 6 of the European Patent EP 0 385 536 B1. This handling is incompatible with the majority of the other process steps where the equipment and transportation tools are developed to handle horizontal positioned substrates.

15 In the United States Patent US 5271774 a spin-drying technique is disclosed which is able to handle horizontal positioned substrates. In fact several small liquid islands are formed being removed from the substrate by a rotary movement. It is known that such a spin-drying technique leaves undesirable residues, often referred to as drying marks, on the substrate surface, particularly on surfaces having mixed hydrophilic and hydrophobic regions.

In the United States Patent US 5660642 a liquid removal technique is disclosed wherein a liquid film present on a surface of a substrate can be removed by applying 25 rinsewater together with a surface tension reducing vapour. Particularly, a disadvantage is that regardless of the precise nature of the liquid, during the liquid removal process always rinsewater is supplied. Furthermore, the surface tension reducing vapour is passively applied, e.g. by natural evaporation, which makes it difficult to locally, i.e. at moving zone, have a good and efficient control on the vapour supply or to direct the vapour. Moreover US 5660642 does not disclose how to remove 30 a liquid film substantially simultaneously from two opposite surfaces, i.e. top and bottomside, of a horizontally positioned substrate. Neither does US 5660642 disclose how to remove efficiently a liquid from the topside of a horizontally positioned substrate.

SUMMARY OF THE INVENTION

In an aspect of the invention a method of removing a liquid from at least one surface of at least one substrate is disclosed, said method comprising the steps of:

- 5 supplying a liquid to said surface of said substrate;
- 10 supplying a gaseous substance to said surface of said substrate, said gaseous substance being at least partially miscible with said liquid and when mixed with said liquid yielding a mixture having a surface tension being lower than that of said liquid; and
- 15 subjecting said substrate to a rotary movement. Said gaseous substance can comprise a substance which when vapourised is miscible with said liquid and when mixed with said liquid yields a mixture having a surface tension being lower than that of said liquid. Said gaseous substance can comprise a gas which is miscible with said liquid and when mixed with said liquid yields a mixture having a surface tension being
- 20 lower than that of said liquid. Said gaseous substance can comprise a mixture of a vapourised substance and a gas, like e.g. helium, argon or nitrogen, said mixture being at least partially miscible with said liquid and when mixed with said liquid yielding a mixture having a surface tension being lower than that of said liquid. Particularly, by supplying said liquid and said gaseous substance on said surface of said substrate, at
- 25 least locally a sharply defined boundary is created between the liquid and the gaseous substance, i.e. a so-called liquid-vapour boundary.

In an embodiment of the invention, said rotary movement is performed at a speed to guide said liquid-vapour boundary over said substrate. Preferably this

- 30 boundary is a curved boundary. The configuration is such that the liquid is kept at the outside of the curved boundary, i.e. at the liquid side of the liquid-vapour boundary.

In an embodiment of the invention the substrate can spin around its own axis. Alternatively said substrate can also be subjected to a rotary movement where said substrate no longer spins around its own centre.

- 35 In another embodiment of the invention, on said surface of said substrate fresh liquid is sprayed continuously. The entire surface at the liquid side of the liquid-vapour boundary can be covered, as e.g. for hydrophilic surfaces, with a continuous film of the liquid. The speed of the rotary movement is chosen such that the flow of said sprayed liquid on at least one side of the wafer is transported outwards due to the centrifugal forces. Moreover, said gaseous substance, when mixed with said liquid yields a mixture having a surface tension being lower than that of said liquid. The resulting surface tension reduction of said liquid facilitates the movement of said liquid towards an edge

of the substrate. The surface left behind is cleaned and dried. It is presumed that this drying action is obtained according to at least the combination of the rotary movement and the Marangoni effect. According to the Marangoni effect said substances will be mixed with the liquid such that in the liquid meniscus, its concentration decreases in the direction of the liquid. This gradient in concentration creates an additional force exerted on the liquid film in the direction of the liquid film resulting in a good drying performance.

The liquid is selected dependent upon the applied wet processing step like e.g. a wet etching step or a cleaning step or a rinsing step. To initiate the drying process, besides said liquid also a gaseous substance reducing the surface tension of said liquid is sprayed on at least one surface of said substrate. Particularly, a pressurized gaseous substance is actively supplied e.g. by using at least one nozzle. Said surface tension reducing gaseous substance can be isopropyl alcohol (IPA), but also any other gaseous substance which is miscible with said liquid and which will form a mixture with said liquid having a surface tension lower than that of said liquid alone, can be used.

In an embodiment of the invention, eventually prior to the liquid removal step an etching, a cleaning or a rinsing liquid or a sequence of such liquids can be supplied to the entire surface of a rotating substrate. The parameters can be optimized such that a liquid film can completely cover a surface. The spinning motion will quickly transport the liquid over the surface towards the edge, thus allowing relatively short carry-over transients and thus also allowing for relatively short rinsing times. Using such a continuously switched flow of liquids eliminates the undesirable passage of liquid-gas interfaces over the surface. The liquid removal method of the present invention is applicable for each sequence of at least one wet processing step by supplying a surface tension reducing gaseous substance together with the liquid. The drying can thus be applied directly on the processing liquid if relevant for the application. Since the proposed drying technique is found to be very fast, process non-uniformity over the surface can be kept very low.

In an aspect of the invention an apparatus for removing a liquid from at least one surface of at least one substrate is disclosed, said apparatus comprising:

- a substrate holder which is subjectable to a rotary movement, said substrate being fixable to said substrate holder;
- a liquid supply system for applying a liquid on said surface of said substrate;
- a gaseous substance supply system for applying a gaseous substance on said surface of said substrate. Preferably, said gaseous substance supply system and said

liquid supply system are positioned such that said gaseous substance is applied closer to the centre of said rotary movement of said substrate holder than said liquid. According to the apparatus of the invention, said gaseous substance supply system can comprise at least one nozzle for applying said gaseous substance on said surface of said substrate and said liquid supply system can comprise at least one nozzle for applying said liquid on said surface of said substrate, said nozzles are positioned such that said gaseous substance is applied closer to the centre of the rotary movement of the substrate holder than said liquid. Particularly, at least locally a sharply defined liquid-vapour boundary can be created which is located inbetween a first and a second adjacent nozzle, said first nozzle being part of said gaseous substance supply system, said second nozzle being part of said liquid supply system. Further according to the apparatus of the invention, said nozzles can be mounted on an arm, said arm being movable relative to said substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts a schematic representation (vertical cross-section) of a tool used for removing a liquid from the topside of a surface of a rotating substrate according to an embodiment of the invention.

Figure 2 a) depicts a schematic representation, i.e. a top view, while fig. 2 b) depicts a cross-section (A-B) of a tool used for removing a liquid from a rotating substrate according to an embodiment of the invention.

Figure 3 a) depicts a top view of the cross-sectional plane (C-D) of fig. 2 b) perpendicular to the surface of the substrate through the point of liquid impingement (30) and perpendicular to the imaginary line connecting the point of liquid impingement and the rotation centre (31) of a tool used for removing a liquid from a rotating substrate according to an embodiment of the invention. The vector representing the velocity of the liquid leaving the nozzle can lie in this cross-sectional plane (C-D) or in a plane (X-Y) perpendicular to the surface of the substrate making a small angle (33) with (C-D), i.e. the liquid velocity vector can be slightly oriented outwards. Figure 3 b) depicts the X-Y plane.

Figure 4 a) depicts a schematic representation, i.e. a top view, while fig. 4 b) depicts a cross-section (E-F) of a tool used for removing a liquid from a rotating substrate according to an embodiment of the invention.

Figure 5 depicts a vertical cross-section of an implementation of a tool according to an embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

In relation to the appended drawings the present invention is described in detail in the sequel. Several embodiments are disclosed. It is apparent however that a person skilled in the art can imagine several other equivalent embodiments or other ways of practising the present invention, the spirit and scope of the present invention being limited only by the terms of the appended claims.

In an aspect of the invention a method of removing a liquid from at least one surface of at least one substrate is disclosed, said method comprising the steps of:

- supplying a liquid to said surface of said substrate;
- supplying a gaseous substance to said surface of said substrate, said gaseous substance being at least partially miscible with said liquid and when mixed with said liquid yielding a mixture having a surface tension being lower than that of said liquid;
- and
- subjecting said substrate to a rotary movement. Said gaseous substance can comprise a substance which when vapourised is miscible with said liquid and when mixed with said liquid yields a mixture having a surface tension being lower than that of said liquid. Said gaseous substance can comprise a gas which is miscible with said liquid and when mixed with said liquid yields a mixture having a surface tension being lower than that of said liquid. Said gaseous substance can comprise a mixture of a vapourised substance and a gas, like e.g. helium, argon or nitrogen, said mixture being at least partially miscible with said liquid and when mixed with said liquid yielding a mixture having a surface tension being lower than that of said liquid. Particularly, by supplying said liquid and said gaseous substance on said surface of said substrate, at least locally a sharply defined liquid-vapour boundary is created. Said boundary has to be such that, at least within the part of the surface which is not rewetted during a subsequent revolution, said boundary is a continuous one, i.e. said part is determined by the lateral movement of said boundary during a revolution. According to the method of the present invention, said rotary movement is performed at a speed to guide said liquid-vapour boundary over said substrate. The configuration is such that the liquid is kept at the liquid side of the liquid-vapour boundary.

According to this method of the invention, on at least one surface, preferably on both opposite surfaces simultaneously i.e. the top and bottomside, of at least one substrate fresh liquid is sprayed continuously. The entire surface at the liquid side of the liquid-vapour boundary can be covered with a film of the liquid. The speed of the rotary movement is chosen such that the flow of said sprayed liquid on said surface of

the wafer is transported outwards due to the centrifugal forces. The rotational speed, the flow of the liquid supply, and the orientation and the velocity at which the liquid arrives on the surface can be optimized in order to result in a liquid film with a sharp and stable liquid-vapour boundary and to keep the thickness of the liquid film small enough to avoid excessive losses of liquid on the bottomside by gravitational forces. Moreover, said gaseous substance when mixed with the liquid, results in a surface tension reduction of said liquid thereby facilitating the movement of said liquid towards an edge of the substrate. The surface left behind is cleaned and dried. It is presumed that this drying action is obtained according to at least the combination of the Marangoni effect and a second force. Preferably this second force is the force introduced by a rotary movement or e.g. an oscillating movement. According to the Marangoni effect said substances will be mixed with the liquid such that in the liquid meniscus, its concentration decreases in the direction of the liquid. This gradient in concentration creates an additional force exerted on the liquid film in the direction of the liquid film resulting in a good drying performance. Particularly, the centre of the rotary movement can coincide with the centre of the substrate, i.e. the substrate spins around its own centre. In this case, if a liquid is sprayed on a surface of a substrate rotating typically with a speed between 2 and 20 revolutions per second, but the invention is not limited thereto, a curved shaped liquid-vapour boundary is created. The entire surface area outside of this curved boundary, can be covered with a film of the liquid. Particularly when using hydrophilic substrates, the entire surface area outside of this curved boundary is covered with a continuous film of the liquid. However also other more complex shaped boundaries can be created, particularly on substrates with a high contact angle for the liquid and if a low flow of liquid is applied. Such complex shaped boundaries will also assist in removing a liquid.

The liquid is selected dependent on the applied wet processing step: for etching steps, e.g. dilute aqueous solutions comprising e.g. HF can be used; for cleaning steps, e.g. a mixture of NH_4OH , H_2O_2 and H_2O or a mixture of HCl , H_2O_2 and H_2O or dilute HCl or a mixture comprising O_3 can be used; for rinsing steps, the rinsing liquid can comprise H_2O , or a mixture of H_2O and an acid, said mixture preferably having a pH between 2 and 6. Preferably said acid is one of the group of HNO_3 , H_2CO_3 , HCO_3 , HCl , HBr , H_3PO_4 , H_2SO_4 . To initiate the removal process, besides said liquid also a gaseous substance is sprayed on at least one surface of said substrate. Said gaseous substance can comprise a substance, like e.g. isopropyl alcohol (IPA), diacetone, ethyllactate, ethylglycol, methylpyrrolidon or a mixture of one of the aforementioned substance, which when vapourised is miscible with said liquid and when mixed with said liquid yields a mixture having a surface tension being lower than that of said liquid

There are several implementations possible to apply both the liquid and the vapour of the surface tension reducing substance on at least one surface of at least one substrate. Preferably the implementation has to be such that initially the gaseous substance is supplied at or very close to the centre of the rotary movement, while the liquid is supplied out of centre but adjacent to the gaseous substance supply. The liquid can also be supplied further away from said centre. By doing so on said surface of said substrate a liquid-vapour boundary can be formed which is initially located at said centre. Then, due to the rotary movement and the movement of the gaseous substance and liquid supply system, this boundary is slowly guided outwards from the centre to the edge to thereby remove the liquid or the solution of said liquid from said surface of said substrate. A sharply defined liquid-vapour boundary, at least locally, is helpful in order to obtain an optimal performance. Contrary to the state of the art, the method of the present invention is perfectly suited to handle a horizontal positioned substrate resulting in a secure and reliable approach which is compatible with substrate handling in most of the other process steps in the manufacturing of integrated circuits. Moreover because, according to the present invention, the liquid of the liquid-vapour boundary is continuously refreshed, besides a good drying performance also a better cleaning performance is obtained simultaneously. A better cleaning performance can be obtained regardless of the precise nature of the liquid, i.e. a wet processing liquid like e.g. a cleaning liquid or a rinsing liquid or a wet etching liquid, as long as the liquid is miscible with the surface tension reducing gaseous substance. Furthermore the required amounts of liquid are substantially lower compared with conventional wet processing baths or tanks.

According to the method of the present invention first the liquid is supplied on a surface of a substrate at or very close to the centre of the rotary movement, while there is no gaseous substance supply. In an embodiment of the invention the centre of the rotary movement coincides with the centre of the substrate, i.e. the substrate spins around its own centre. Then the gaseous substance supply system, e.g. a nozzle is moved to the centre of the rotary movement, i.e. the centre of the substrate, and the pressurised gaseous substance is supplied actively at said centre while the liquid is supplied slightly out of centre. The liquid can also be supplied further away from said centre. By doing so on said surface of said substrate a liquid-vapour boundary is formed which is initially located at said centre. Then, due to the rotary movement and the movement of the gaseous substance and liquid supply system, this boundary is slowly guided outwards from the centre to the edge of said surface of said substrate to

thereby remove the liquid or the solution of said liquid from said surface of said substrate.

In an aspect of the invention an apparatus for removing a liquid from at least one surface of at least one substrate is disclosed, said apparatus comprising:
 5 a substrate holder (1) (11) which is subjectable to a rotary movement, said substrate (2) being fixable to said substrate holder;
 a liquid supply system (5) for applying a liquid on said surface of said substrate;
 10 a gaseous substance supply system (4) for applying a gaseous substance on said surface of said substrate. Preferably, said gaseous substance supply system and said liquid supply system are positioned such that said gaseous substance is applied closer to the centre of said rotary movement of said substrate holder than said liquid.

15 In an embodiment of the invention, as illustrated in figure 1, a substrate (2) is placed on a revolving substrate holder (1). Said substrate can be placed in a chamber of a tool comprising at least one chamber. Said substrate holder and the substrate thereon are rotating with a speed which is typically between 2 and 20 or more revolutions per second. A movable arm (3), which can be guided between the centre
 20 and the edge of the substrate extends above the topside of the substrate. Initially one end of this arm is located near the centre of the rotary movement, i.e. the centre of the substrate. Said arm comprises at least two supply systems, a first supply system comprising means (4) for supplying a surface tension reducing gaseous substance to the substrate, a second supply system comprising means (5) for supplying a liquid to the
 25 substrate. Said first supply system further comprises at least one nozzle, initially being placed at or near the centre of the substrate, for spraying said gaseous substance on said substrate. Said second supply system further comprises at least one nozzle, being placed more outwards than said nozzle for spraying gaseous substance, for spraying said liquid on said substrate. Alternatively, instead of a movable arm comprising fixed
 30 nozzles also movable nozzles on a fixed arm can be used. To ensure that each part of the substrate is effectively dried, the translation speed, v , at which the arm, i.e. the nozzles, moves can be adapted to the rotational (angular) speed, ω , of the substrate. Suppose that Δr is the translation distance, being the radial distance over which the liquid-vapour boundary extends radially during one revolution, then the rotational
 35 speed can be chosen such that:

$$\Delta r = \frac{2\pi \cdot v}{\omega}$$

For example, suppose that the translation distance per revolution, Δr , equals 1 mm and that the translation speed, v , equals 1 mm per second, then the rotational speed is 1 revolution per second.

In tests, the nozzles are located such that their centre lines will draw concentric circles on the surface with a difference in radius on the order of 5 mm. By doing so, at the topside of the substrate a curved liquid-vapour boundary is formed which is initially located at said centre of the substrate. Then this boundary is slowly guided outwards by moving said arm (3) from the centre to the edge of the substrate to thereby remove the liquid or the solution of said liquid from the topside of said substrate. The liquid-vapour boundary is located in between the nozzle providing the surface tension reducing gaseous substance and the nearest nozzle spraying the liquid. Using this method fresh liquid with very low concentration of the surface tension reducing gaseous substance is supplied at the liquid-vapour boundary thus maximizing the removal of the liquid (maximizing Marangoni force). In figure 1 the nozzles (6) are placed such that the gaseous substance is sprayed perpendicular, i.e. at an angle of 90° , on the substrate and also the liquid is sprayed on the substrate. Spraying the liquid can be done such that at least locally a sharp and stable curved boundary is obtained, and particularly in case hydrophilic substrates are used the entire surface of the substrate at the outside of the boundary is kept wet. This will involve optimization of the orientation of the liquid nozzle(s) and of the velocity of the liquid leaving the nozzle. In order to limit splashing of the liquid the angle (32) between the velocity vector of the liquid (figure 3 (13)) when leaving the nozzle and the velocity vector of the rotating surface (figure 3 (14)) at the point (30) where the liquid flow impinges can be kept small. Eventually, the liquid nozzles can also be slightly oriented outwards, i.e. typically at an angle (33) between 0 degrees and 5 degrees. For removing a liquid having a low contact angle in contact with the surface, it is found sufficient to have only one nozzle for supplying the liquid. In case of higher contact angles, in order to maintain a wet substrate surface outside the drying boundary, additional nozzles for spraying liquid can be installed at equal or greater distance from the rotation centre (31). In order to further limit the consumption of the liquid the additional nozzles can be turned off as they move over the substrate edge. It may be useful to progressively modulate the flow and the rotation speed as the drying proceeds from the centre towards the edge of the substrate.

According to this embodiment of the invention, as an example, experiments are performed using such an apparatus for removing a liquid from the topside of a substrate. Particularly, the gaseous substance supply system of said apparatus comprises one nozzle and the liquid supply system of said apparatus also comprises

one nozzle. Said nozzles are mounted on an arm, said arm being movable relative to said substrate. The substrates used in the experiments are silicon wafers with a diameter of 150 mm with a deposited oxide layer on top. The thickness of the oxide layer is 1.1 μm . The wafers are polished by means of chemical mechanical polishing. After this treatment, the thickness of the remaining oxide layer is 700 nm. Immediately thereafter the wafers are put in a water container.

In a first experiment a state of the art method is used to remove the water from the topside of a wafer. The wafer is placed on a substrate holder and subjected to a rotary movement at a speed of 600 revolutions per minute during 40 seconds while only a surface tension reducing gaseous substance, i.e. a mixture of vapourised isopropyl alcohol (IPA) and nitrogen, is supplied. The experiment is performed in a class 10000 cleanroom area. After this removal treatment light point-defects (LPD's), being a measure for the number of contamination particles, are measured using a Tencor Surfscan 6400. The number of LPD's per wafer measured with a polystyrene latex sphere equivalent (PSLSE) diameter between 0.2 and 0.3 μm is 309 with a standard deviation of 113. These numbers are an average of LPD measurements on two different wafers which were subjected to the same treatment according to this first experiment.

In a second experiment, according to this embodiment of the present invention a method is used to remove the water from the topside of a wafer. The wafer is placed on a substrate holder and subjected to a rotary movement at a speed of 600 revolutions per minute during 15 seconds or 25 seconds. A pressurized surface tension reducing gaseous substance, i.e. a mixture of vapourised isopropyl alcohol (IPA) and nitrogen, is actively supplied by the first nozzle, while a liquid, i.e. fresh water, is actively supplied by the second nozzle. The arm comprising the nozzles is moved from the centre to the edge with a radial velocity of 5 mm per second or 3 mm per second. The experiment is performed outside a cleanroom area. After this removal treatment light point-defects (LPD's), being a measure for the number of contamination particles, are measured using a Surfscan 6400. The number of LPD's per wafer measured with a PSLSE diameter between 0.2 and 0.3 μm is 14 with a standard deviation of 5. These numbers are an average of LPD measurements on six different wafers, 3 which are subjected to the same treatment, i.e. with a radial velocity of 5 mm per second, and the other three wafers which are also subjected to the same treatment, i.e. with a radial velocity of 3 mm per second according to this second experiment. From the LPD measurements it is clear that the method of the present invention has a better cleaning and drying performance, particularly with regard to particles.

In an embodiment of the invention, as illustrated in figure 2, a substrate (2) can be clamped into a ring-shaped substrate holder (11) having an inner diameter larger

than the diameter of the substrate. The clamping is done using minimal contact surface. The substrate holder or alternatively the substrate itself is placed between at least two revolving means (12) which transmit the rotational force to said substrate holder comprising the substrate or alternatively to said substrate alone. Said substrate holder
 5 comprising said substrate or said substrate alone can be placed in a chamber of a tool comprising at least one chamber. Said substrate is rotating with a speed which is typically between 2 and 40 revolutions per second. Two movable arms (3), which can be guided separately or simultaneously between the centre and the edge of the substrate extend above the topside and below the bottomside of the substrate. Initially
 10 one end of each of these arms is located near the centre of the substrate. Each of these arms comprises at least two supply systems, a first supply system comprising means (4) for supplying a surface tension reducing gaseous substance to the substrate, a second supply system comprising means (5) for supplying a liquid to the substrate. Said first supply system further comprises at least one nozzle, being placed near the
 15 centre of the substrate, for spraying said gaseous substance on said substrate. Said second supply system further comprises at least one nozzle, being placed more outwards than said nozzle for spraying gaseous substance, for spraying said liquid on said substrate. By doing so both at the topside and on the bottomside of the substrate a liquid-vapour boundary can be formed which is located at said centre of the
 20 substrate. Then this boundary is slowly guided outwards by moving said arms (3) from the centre to the edge of the substrate to thereby remove the liquid or the solution of said liquid from the surfaces of said substrate. In order to limit splashing of the liquid the angle between the velocity of the liquid (figure 3 (13)) when leaving the nozzle and the velocity of the rotating surface (figure 3 (14)) at the point where the liquid flow
 25 impinges can be kept small.

Another approach for building this rotation system is shown in figure 4. In this case the arm (18) at the bottomside is mounted on a central shaft (15). Around this shaft a hollow shaft (16) is rotating. On this hollow shaft the clamping means (17) of the
 30 substrate are fixed. The arms moving over a radius of the substrate can be made compact, i.e. like a man's arm. The arm on the topside can be similar, but no rotation gear is required at the topside.

In an embodiment of the invention (fig. 5), the liquid supply system (3)
 35 comprises a cup-shaped nozzle (51) which can be guided over the rotating substrate (2) and which is positioned very close to a surface of a substrate. Particularly, the distance between this cup-shaped nozzle and a surface of the substrate is typically about 0.5 mm. The liquid, e.g. water, can be supplied through the cup.

In tests, according to the method of the invention, the nozzles are positioned in order to draw concentric circles on the surface with a difference in radius in the order of 6 mm. One nozzle is provided to spray the liquid, i.e. H_2O on a surface of a 150 mm silicon wafer. The rate of the liquid flow is about 60 ml per minute. The surface tension reducing gaseous substance used is a mixture of vapourised IPA and a nitrogen gas. The rotation speed is about 300 revolutions per minute. These conditions are suited to remove the liquid very efficiently for hydrophilic wafers. It is found that particularly for hydrophobic silicon wafers, it is important to have a sufficiently high liquid supply to keep the outer parts of the wafer wet. Preferably additional nozzles can be provided to ensure this.

According to the method of the present invention, the same rotation station can be used to perform a wet chemical processing step like e.g. a wet etching step, wet cleaning and rinsing a substrate, or to perform an arbitrary sequence of such wet processing steps. In an embodiment of the invention, prior to the initiation of the liquid removal process, i.e. prior to supplying a surface tension reducing gaseous substance, an etching, cleaning or rinsing liquid or a continuous sequence of such liquids can be supplied to at least one surface of the substrate. For example, this can be done by using at least one of the liquid nozzles (and eventually additional nozzles further away from the centre). The parameters can be optimized such that a continuous liquid film is present on the surface. The spinning motion will quickly transport the liquid over the surface towards the edge, thus allowing relatively short carry-over transients and thus also allowing for relatively short rinsing times. Using such a continuously switched flow of liquids eliminates the passage of liquid-gas interfaces over the surface. The liquid removal method of the present invention is applicable for each sequence of at least one wet processing step by supplying a surface tension reducing gaseous substance together with the liquid. The removal method can thus be applied directly on the processing liquid if beneficial for the application. Since the proposed removal method is found to be very fast, process non-uniformity over the surface, i.e. centre to edge or edge to edge, can be kept very low.

WHAT IS CLAIMED IS:

1.
A method of removing a liquid from at least one surface of at least one substrate
5 comprising the steps of:
supplying a liquid to said surface of said substrate;
supplying a gaseous substance to said surface of said substrate, said gaseous
substance being at least partially miscible with said liquid and when mixed with said
liquid yielding a mixture having a surface tension being lower than that of said liquid;
10 and
subjecting said substrate to a rotary movement.
2.
A method as recited in claim 1, wherein, by supplying said liquid and said gaseous
15 substance on said surface of said substrate, at least locally a sharply defined liquid-
vapour boundary is created.
3.
A method as recited in claim 1, wherein said rotary movement is performed at a speed
20 to guide said liquid-vapour boundary over said substrate.
4.
A method as recited in claim 3, wherein said rotary movement is applied such that the
substrate spins around its own centre.
- 25 5.
A method as in claim 4, wherein the rotation speed is in the range from 2 to 40
revolutions per second.
- 30 6.
A method as recited in claim 1, wherein said gaseous substance comprises a substance
which when vapourised is miscible with said liquid and when mixed with said liquid
yields a mixture having a surface tension being lower than that of said liquid.
- 35 7.
A method as recited in claim 6, wherein said substance is selected from a group
comprising isopropyl alcohol (IPA), diacetone, ethylglycol, ethyllactate and
methylpyrrolidon or a mixture thereof.

8.

A method as recited in claim 1, wherein said gaseous substance comprises a mixture of a vapourised substance and a gas, said mixture being at least partially miscible with said liquid and when mixed with said liquid yielding a mixture having a surface tension being lower than that of said liquid.

9.

A method as recited in claim 8, wherein said substance is selected from a group comprising isopropyl alcohol (IPA), diacetone, ethylglycol and methylpyrrolidon or a mixture thereof and said gas is an inert gas.

10.

A method as recited in claim 1, wherein said gaseous substance comprises a gas which is miscible with said liquid and when mixed with said liquid yields a mixture having a surface tension being lower than that of said liquid.

11.

A method as recited in claim 1, wherein said liquid is one of a group of an etching liquid, a cleaning liquid or a rinsing liquid.

12.

A method as recited in claim 11, wherein said etching liquid is a dilute aqueous solution.

13.

A method as recited in claim 11, wherein said cleaning liquid comprises a mixture of NH_4OH , H_2O_2 and H_2O ; or comprises a mixture of HCl , H_2O_2 and H_2O ; or comprises diluted HCl ; or comprises a mixture comprising O_3 .

14.

A method as recited in claim 11, wherein said rinsing liquid comprises H_2O ; or a mixture of H_2O and an acid, said mixture having a pH between 2 and 6.

15.

A method as recited in claim 1, wherein said liquid and said gaseous substance are supplied substantially simultaneously.

16.

A method of removing substantially simultaneously a liquid from a first side and a second side of at least one substrate comprising the steps of:

5 substantially simultaneously supplying a liquid to said first side and said second side of said substrate;

substantially simultaneously supplying a gaseous substance to said first side and said second side of said substrate, said gaseous substance being at least partially miscible with said liquid and when mixed with said liquid yielding a mixture having a surface tension being lower than that of said liquid; and
10 subjecting said substrate to a rotary movement.

17.

A method as recited in claim 16, wherein said first side is the topside and said second side is the bottomside of said substrate.

18.

An apparatus for removing a liquid from at least one surface of at least one substrate, said apparatus comprising:

20 a substrate holder which is subjectable to a rotary movement, said substrate being fixable to said substrate holder;

at least one liquid supply system for applying a liquid on said surface of said substrate;

25 at least one gaseous substance supply system for applying a gaseous substance on said surface of said substrate.

19.

An apparatus as recited in claim 18, where said gaseous substance supply system and said liquid supply system are positioned such that said gaseous substance is applied closer to the centre of said rotary movement of said substrate holder than said liquid.

20.

35 An apparatus as recited in claim 18, where said gaseous substance supply system comprises at least one nozzle for applying said gaseous substance on said surface of said substrate and said liquid supply system comprises at least one nozzle for applying said liquid on said surface of said substrate, said nozzles are positioned such that said gaseous substance is applied closer to the centre of the rotary movement of the substrate holder than said liquid.

21.

An apparatus as recited in claim 18, where said nozzles are mounted on an arm, said arm being movable relative to said substrate.

5

22.

An apparatus for removing a liquid from a first side and a second side of at least one substrate, said apparatus comprising:

10 a substrate holder which is subjectable to a rotary movement, said substrate being fixable to said substrate holder;

a first and a second liquid supply system, said first liquid supply system for applying a liquid on said first side of said substrate and said second liquid supply system for applying a liquid on said second side of said substrate;

15 a first and a second gaseous substance supply system, said first gaseous substance supply system for applying a gaseous substance on said first side of said substrate and said second gaseous substance supply system for applying a gaseous substance on said second side of said substrate.

ABSTRACT

METHOD OF REMOVING A LIQUID FROM A SURFACE OF A ROTATING SUBSTRATE

5

A method of removing a liquid, i.e. a wet processing liquid, from a surface of at least one substrate is disclosed. A liquid is supplied on a surface of substrate. Simultaneously or thereafter besides the liquid also a gaseous substance can be supplied thereby creating at least locally a sharply defined liquid-vapour boundary.

10 The gaseous substance and the liquid can be selected such that the gaseous substance is miscible with the liquid and when mixed with the liquid yields a mixture having a surface tension lower than that of the liquid. According to the invention, the substrate is subjected to a rotary movement at a speed to guide said liquid-vapour boundary over said substrate thereby removing said liquid from said substrate.

15

THE UNITED STATES OF AMERICA
DO hereby certify that the within and foregoing is a true and correct copy of the original as the same appears in the records of the Department of the Interior.

WITNESSED my hand and the seal of the Department of the Interior at Washington, D.C., this 1st day of January, 1902.

JOHN W. FOSTER, Secretary of the Interior.

By _____, Deputy Secretary of the Interior.



Figure 1

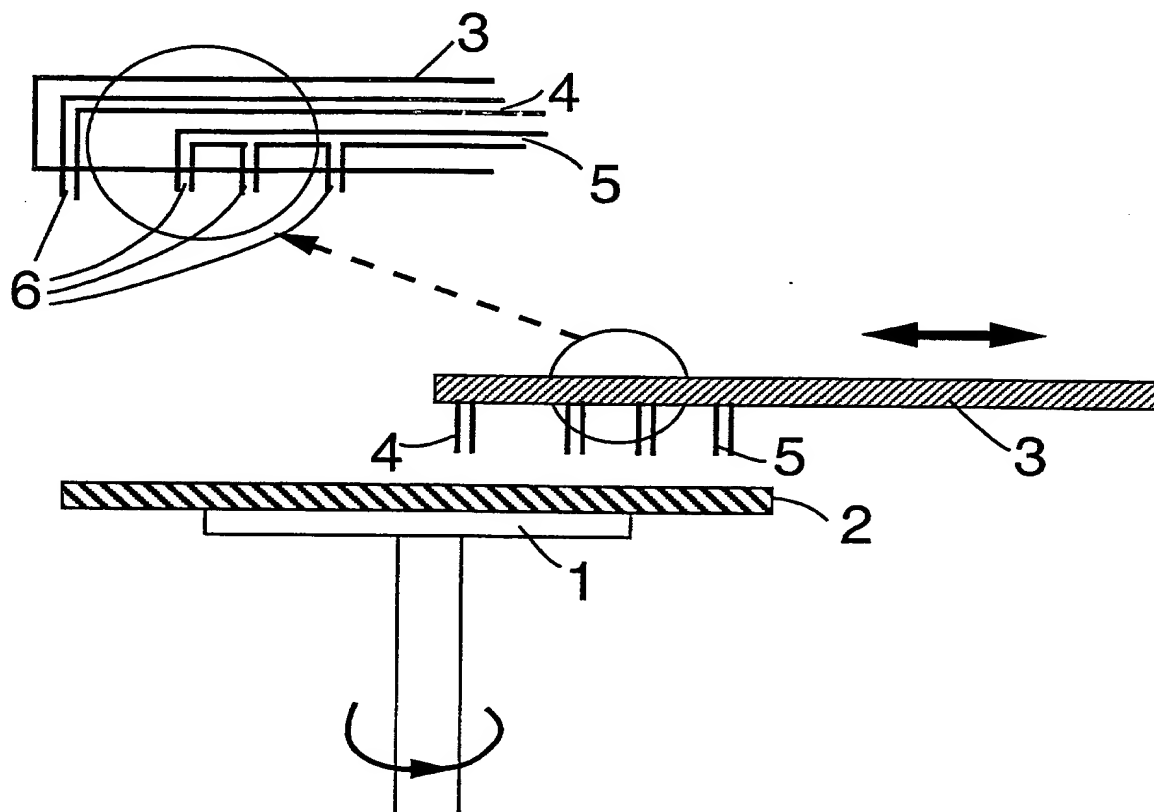


Figure 2

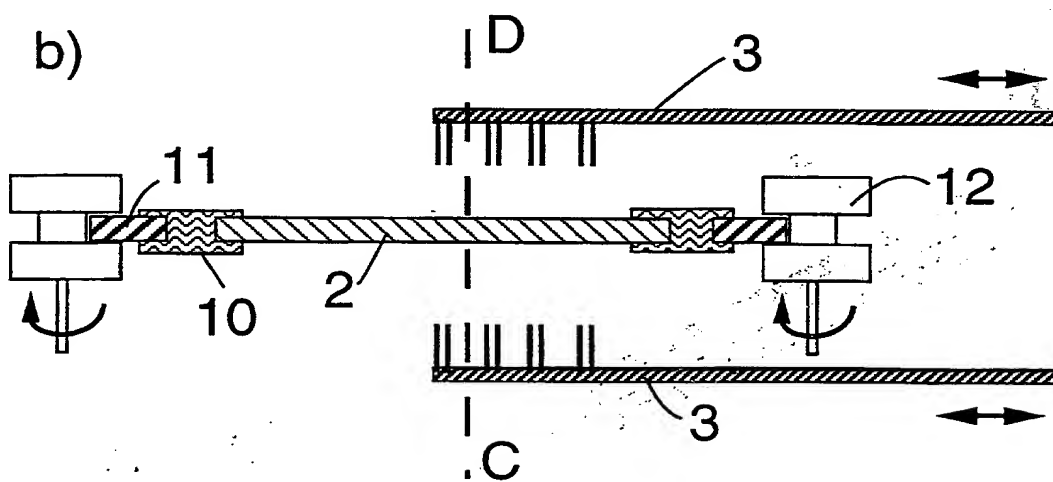
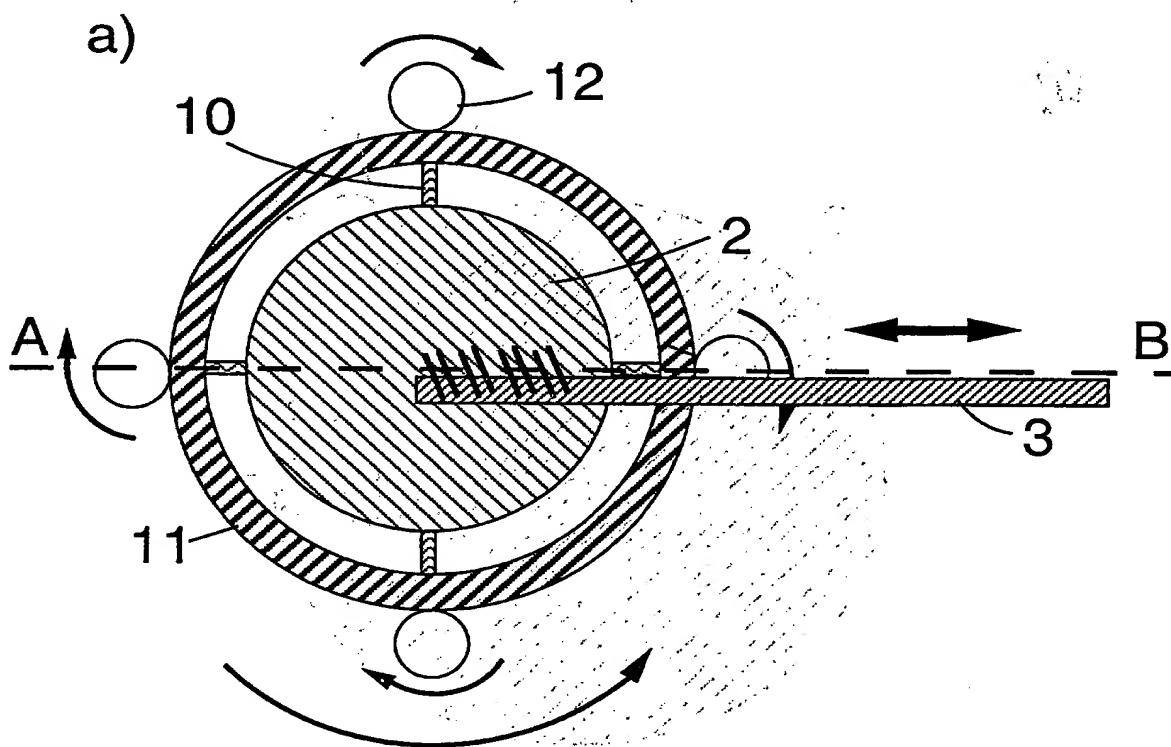
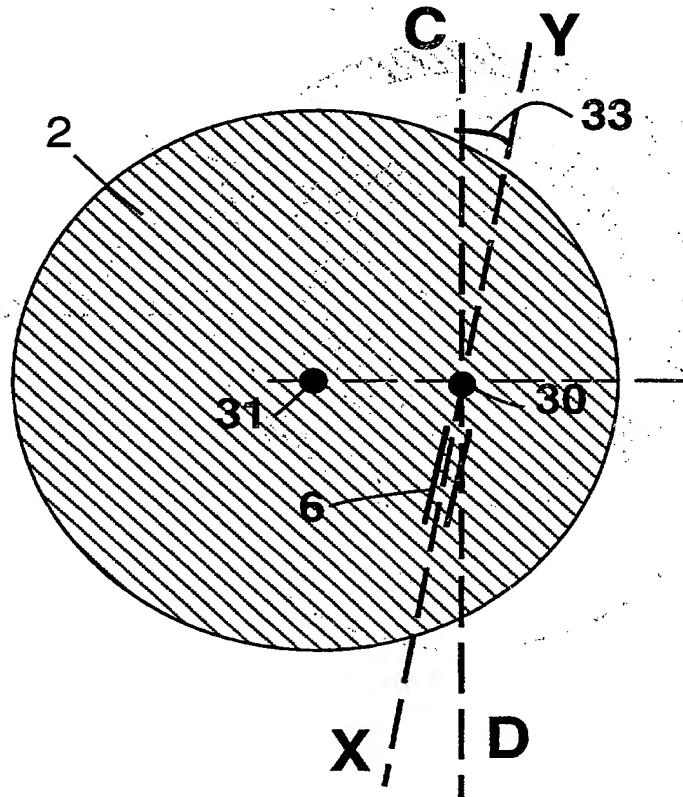


Figure 3

a)



b)

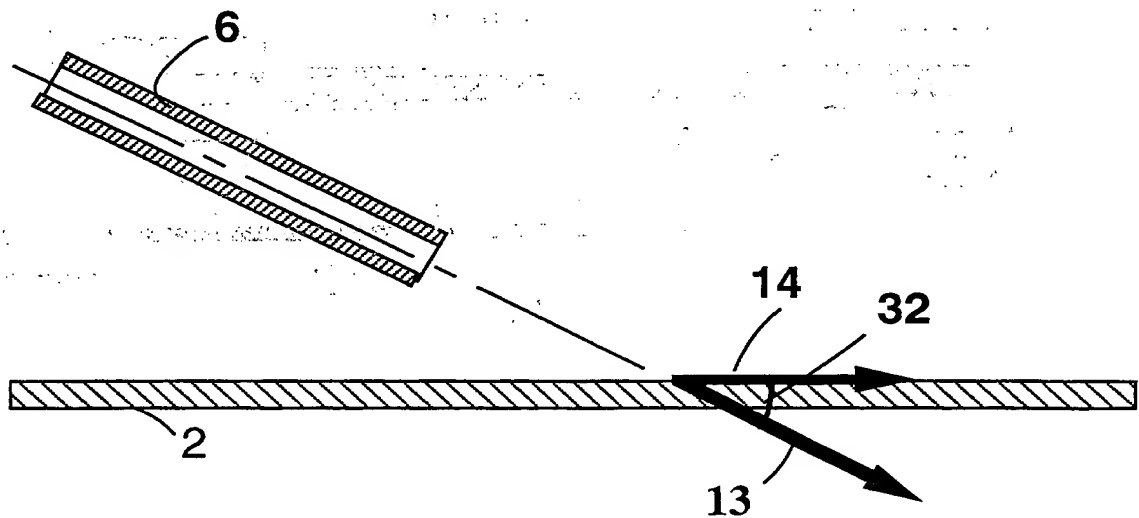
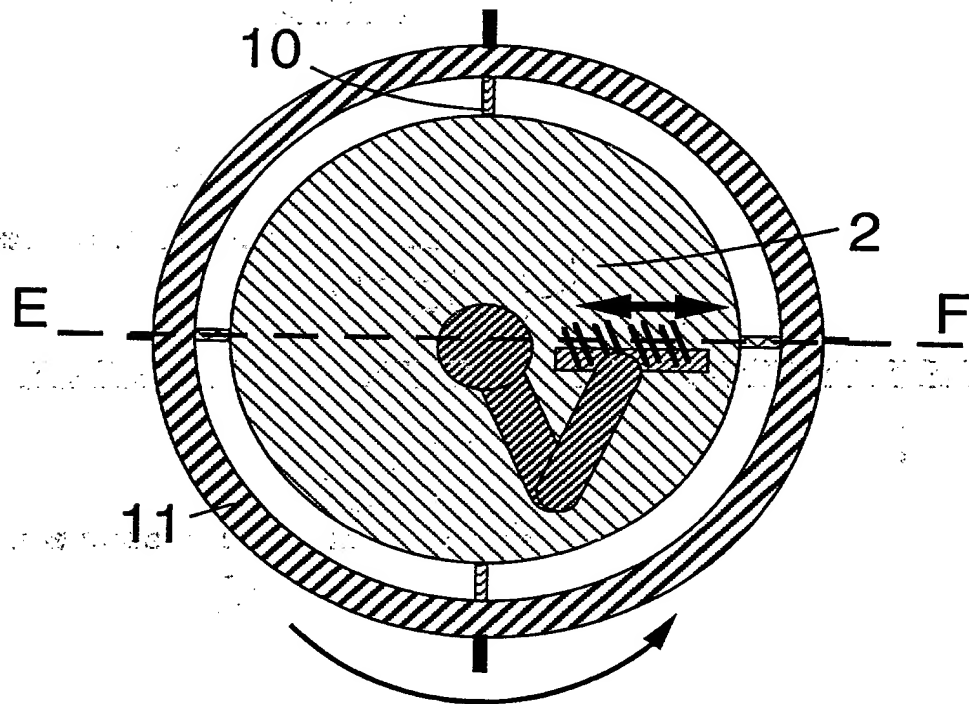


Figure 4

a)



b)

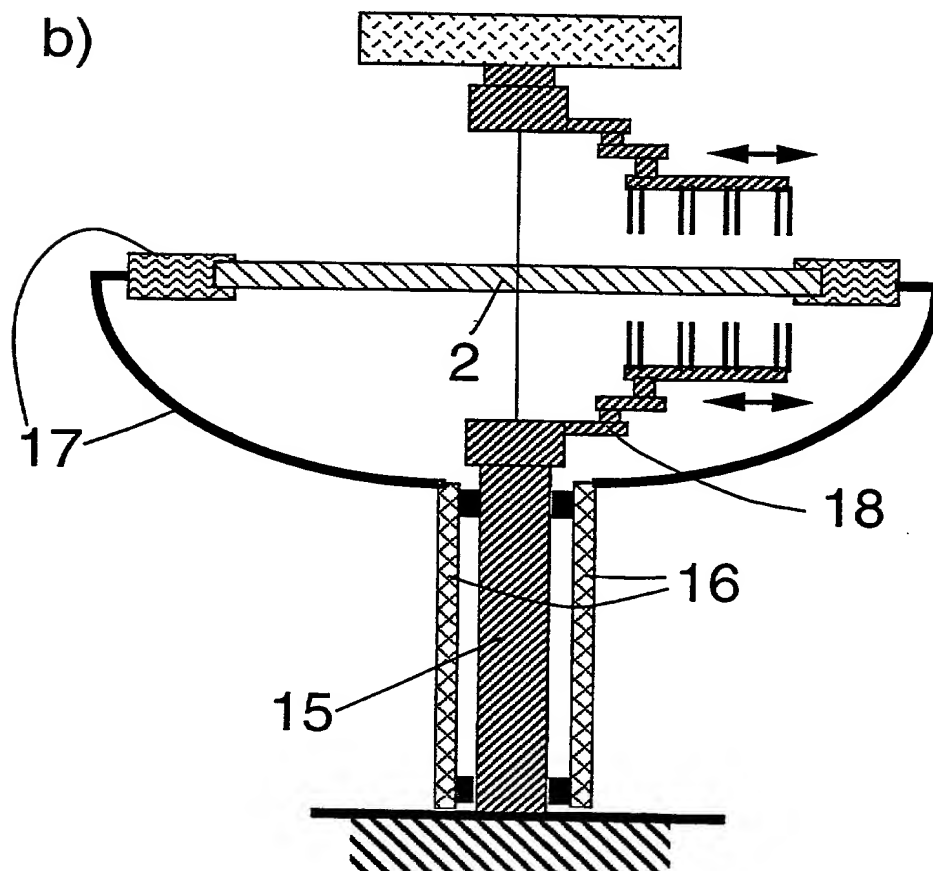


Figure 5